Supporting Information

19.35%-Efficiency organic solar cells and reduced non-radiative recombination energy loss by ternary copolymerization strategy

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1. Energy level calculation

The geometries of the ground states for DTBT and TQC units were optimized by density functional theory at the B3LYP/6-31G(d, p) level implemented in Gaussian-16 software.^[1]



Fig. S1 Calculated HOMO and LUMO energy levels of DTBT and TQC units.

2. Materials

Unless stated otherwise, all solvents and chemical reagents were obtained commercially and used without further purification. All reactions dealing with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques. F-BDT-Sn and DTBT-Br were purchased from SunaTech Inc. and Derthon Co., respectively. L8-BO and D18 were purchased from Hyper Inc. and Derthon Co., respectively. Dimethyl 2,3-dioxosuccinate and benzo[2,1-b:3,4-b']dithiophene-4,5-diamine was synthesized according to the literatures.^[2,3]



Fig. S2 Chemical structure of L8-BO.

3. Synthesis



Fig. S3 Synthetic routes of polymer donors.

Compound 1. Compound 1 was synthesized according to the literatures.^[3] ¹H NMR (400 MHz, DMSO, δ /ppm): 7.60 (d, J = 5.4 Hz, 1H), 7.45 (d, J = 5.4 Hz, 1H), 4.85 (s, 2H).

Compound 2 (TQC). Compound 1 (480 mg, 2.17 mmol) and dimethyl 2,3-dioxosuccinate (1511 mg, 8.68 mmol) was added into acetic acid (10 mL) under an nitrogen atmosphere. The resulting mixture was heated to 100 °C and stirred for overnight. After cooling to room temperature, the mixture was poured into ice water and extracted with CH_2Cl_2 . The organic phase was washed with water and dried over anhydrous Na_2SO_4 and filtrated. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether: CH_2Cl_2 (1:4) as eluent to give compound **2** (**TQC**) as a yellow solid (453 mg, 58%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.37 (d, J = 5.3 Hz, 1H), 7.62 (d, J = 5.3 Hz, 1H), 4.11 (s, 3H).

Compound 3. To a solution of compound **2** (300 mg, 0.84 mmol) in a mixed solvent of CHCl₃ (15 mL) and acetic acid (5 mL) was added *N*-bromosuccinimide (NBS) (360 mg, 2.02 mmol) under an nitrogen atmosphere. The mixture was stirred under dark at 45 °C overnight. Then it was poured into water and extracted with CH₂Cl₂. The organic phase was dried over anhydrous Na₂SO₄ and filtrated. Then the solution was dropped into methanol and filtered to obtain compound **3** as a yellow solid (337 mg, 78%). The compound **3** was used for next step directly without further purification. ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.34 (s, 1H), 4.10 (s, 3H).

Compound 4. An air-free flask was charged with compound **3** (100 mg, 0.19 mmol), (4-(2-butyloctyl)thiophen-2-yl)tributylstannane (309 mg, 0.57 mmol), Pd(PPh₃)₄ (22 mg, 0.019 mmol), and toluene (10 mL). The reaction mixture was stirred at 110 °C for 16 h, then the solvent was removed by evaporation to afford a dark yellow solid, which was purified by column chromatography (silica gel) with CH₂Cl₂:hexane (1:1) as eluent to afford compound **4** as a red solid (125 mg, 75%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.33 (s, 2H), 7.21 (s, 2H), 6.93 (s, 2H), 4.12 (s, 6H), 2.57 (d, *J* = 6.8 Hz, 4H), 1.71–1.59 (m, 6H), 1.42–1.21 (m, 49H), 1.01–0.80 (m, 21H).

QC. To a solution of compound **4** (100 mg, 0.12 mmol) in a mixed solvent of CHCl₃ (15 mL) and acetic acid (5 mL) was added *N*-bromosuccinimide (NBS) (48 mg, 0.27 mmol) under an nitrogen atmosphere. The mixture was stirred under dark at room temperature overnight. Then it was poured into water and extracted with CH₂Cl₂. The organic phase was dried over anhydrous Na₂SO₄ and filtrated. Then, the solvent was removed by evaporation to afford an orange solid, which was purified by column chromatography (silica gel) with CH₂Cl₂:hexane (1:2) as eluent to give **QC** as an orange solid (98 mg, 83%). ¹H NMR (400 MHz, CDCl₃, δ /ppm): 8.29 (s, 2H), 7.06 (s, 2H), 4.12 (s, 6H), 2.53 (d, *J* = 7.1 Hz, 4H), 1.70 (s, 2H), 1.35–1.26 (m, 32H), 0.90 (q, *J* = 6.7 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃, δ /ppm): 164.46, 141.71, 141.02, 136.19, 136.12, 134.51, 134.49, 133.95, 125.77, 118.72, 109.71, 52.48, 37.58, 33.28, 32.35, 32.07, 30.94, 28.73, 27.80, 25.54, 22.10, 21.73, 13.19.

DQ20. To a mixture of DTBT-Br (36.30 mg, 0.04 mmol), **QC** (10.18 mg, 0.01 mmol), FBDT-Sn (47.05 mg, 0.05 mmol), $Pd_2(dba)_3$ (1.37 mg, 0.0015 mmol) and $P(o-tol)_3$ (4.57 mg, 0.015 mmol) in a Schlenk flask was added toluene (1.5 mL) under argon. The mixture was heated to reflux for 8 h/16 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane, CH_2Cl_2 , $CH_2Cl_2/CHCl_3$ (v/v = 1/1) and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane, CH_2Cl_2 , $CH_2Cl_2/CHCl_3$ (v/v = 1/1) and chlorobenzene in sequence.

DQ40. To a mixture of DTBT-Br (27.22 mg, 0.03 mmol), **QC** (20.35 mg, 0.02 mmol), FBDT-Sn (47.05 mg, 0.05 mmol), $Pd_2(dba)_3$ (1.37 mg, 0.0015 mmol) and $P(o-tol)_3$ (4.57 mg, 0.015 mmol) in a Schlenk flask was added toluene (1.5 mL) under argon. The mixture was heated to reflux for 8 h/16 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction by using methanol, hexane, CH_2Cl_2 and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **DQ40** (56 mg, 80%).

4. NMR spectra















5. Cyclic voltammetry



Fig. S11 Cyclic voltammograms of D18, DQ20 and DQ40.



Fig. S12 Cyclic voltammogram of L8-BO.

Table S1. Optical and electrochemical data of D18, DQ20, DQ40 and L8-BO.

	λ_{film}	λ_{onset}	$E_{\rm g}^{\rm opt}$	E_{or}^{on} [V]	E_{rod}^{on} [V]	HOMO	LUMO	$E_{\rm g}^{\rm ec}$
	[nm]	[nm]	$[eV]^a$			[eV]	[eV]	$[eV]^b$
D18	580	630	1.97	0.50	-2.10	-5.30	-2.70	2.60
DQ20	575	632	1.96	0.53	-2.02	-5.33	-2.78	2.55
DQ40	573	634	1.96	0.56	-1.91	-5.36	-2.89	2.47
L8-BO	803	892	1.39	0.74	-1.10	-5.54	-3.70	1.84

 $\overline{{}^{a}E_{g}^{opt} = 1240/\lambda_{onset}; HOMO} = -(E_{ox}^{on} + 4.80); LUMO = -(E_{red}^{on} + 4.80); {}^{b}E_{g}^{ec} = LUMO-HOMO.$

6. Solubility



Fig. S13 Solubility of D18 (4.59 mg mL⁻¹), DQ20 (7.53 mg mL⁻¹), and DQ40 (18.69 mg mL⁻¹) solution in chloroform at 80 $^{\circ}$ C for 30 min.

7. Contact angles

According to the contact angles, the surface tension of polymer donors and L8-BO can be calculated by using the Wu's model.

$$\gamma_{water}(1 + \cos \theta_{water}) = \frac{4\gamma_{water}^{d}\gamma^{d}}{\gamma_{water}^{d} + \gamma^{d}} + \frac{4\gamma_{water}^{p}\gamma^{p}}{\gamma_{water}^{p} + \gamma^{p}}$$
(1)
$$\gamma_{GL}(1 + \cos \theta_{GL}) = \frac{4\gamma_{GL}^{d}\gamma^{d}}{\gamma_{GL}^{d} + \gamma^{d}} + \frac{4\gamma_{GL}^{p}\gamma^{p}}{\gamma_{GL}^{p} + \gamma^{p}}$$
(2)
$$\gamma^{total} = \gamma^{d} + \gamma^{p}$$
(3)

where γ^{total} is the total surface tension of polymer or L8-BO, γ^d and γ^p are the dispersion and polar components of γ^{total} , γ_i is the total surface tension of the *i* material (*i* = water or glycerol), γ_i^d and γ_i^p are dispersion and polar components of γ_i , and θ is the droplet contact angle (water or glycerol) on the polymer or L8-BO film.

Surface	$\theta_{\text{water}}[^{\circ}]$	$\theta_{\mathrm{glycerol}}[^{\circ}]$	$\gamma[mN m^{-1}]$	$\left(\sqrt{\gamma_{polymer}} - \sqrt{\gamma_{L8-B0}}\right)^2$
D18	107.45	91.90	22.94	0.27
DQ20	103.55	87.80	24.43	0.14
DQ40	100.60	84.00	26.53	0.03
L8-BO	95.60	79.30	28.20	

Table S2. Contact angles and surface tension of polymer donors and L8-BO.

8. SCLC

Charge carrier mobility was obtained by using SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of electron (μ_e) or hole (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage, $V = V_{appl} - V_{bi}$ (V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by the electrode work function difference.).



Fig. S14 Typical current density-applied voltage log plots for electron-only devices (a) and hole-only devices (b) based on D18:L8-BO, DQ20:L8-BO and DQ40:L8-BO blend films under dark. The measured data are shown as symbols, while the dashed lines are the best fits to the SCLC model. Mobilities were extracted from the fitting. (c) *J-V* characteristics of hole-only devices based on D18:L8-BO, DQ20:L8-BO and DQ40:L8-BO (n represents the slope of the fitting line.) for trap density.

9. GIWAXS

<i>d</i> -spacing for D18, DQ20 and DQ40 neat films.						
	q (Å ⁻¹)	FWHM (Å)	<i>d</i> -spacing (Å)	CCL (Å)		
D18	1.65	0.44	3.81	12.9		
DQ20	1.65	0.38	3.81	14.9		
DQ40	1.62	0.53	3.88	10.7		

Table S3. Crystal coherence length (CCL) of π - π stacking diffraction peaks and corresponding *d*-spacing for D18, DQ20 and DQ40 neat films.

Table S4. Crystal coherence length (CCL) of π - π stacking diffraction peaks and corresponding *d*-spacing for D18:L8-BO, DQ20:L8-BO and DQ40:L8-BO blend films.

	q (Å-1)	FWHM (Å)	d-spacing (Å)	CCL (Å)
D18:L8-BO	1.73	0.37	3.63	15.3
DQ20:L8-BO	1.73	0.35	3.63	16.2
DQ40:L8-BO	1.73	0.44	3.63	12.9

10. AFM



Fig. S15 AFM height images of (a) D18:L8-BO, (b) DQ20:L8-BO and (c) DQ40:L8-BO blend films. AFM phase images of (d) D18:L8-BO, (e) DQ20:L8-BO and (f) DQ40:L8-BO blend films.



Fig. S16 The line profiles along the white lines to obtain the nano-grain size in (a) D18:L8-BO and (b) DQ20:L8-BO. The nano-grain size is obtained from FWHM (the distance between two adjacent dashed lines in the graphs).

11. Device fabrication and measurements

The devices were fabricated on ITO glass with a structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. PEDOT:PSS layer was deposited onto the ITO glass via spin-coating with 4000 rpm in air for 30 s. The films were annealed at 150 °C in air for 10 min. The donor:L8-BO (1:1.8 w/w) blends were dissolved in CHCl₃ with/without 10 mg/mL 1-bromo-3,5-dichlorobenzene as the solid additive. Among them, the concentrations of D18, DQ20 and

DQ40 are 4 mg mL⁻¹, 5 mg mL⁻¹and 6 mg mL⁻¹ in solution, respectively. The total concentrations of D18:L8-BO, DQ20:L8-BO and DQ40:L8-BO blend solutions are 11.2 mg mL⁻¹, 14.0 mg mL⁻¹ and 16.8 mg mL⁻¹. It should be noted that the blends were dissolved in chloroform under 80 °C for 1 h before device fabrication. The active layer was deposited onto PEDOT:PSS layer via spin-coating with 3000 rpm for 30 s in the nitrogen glove box, then annealed under 100 °C in N₂ for 10 min. PDINN in MeOH (1 mg mL⁻¹) was deposited onto active layer via spin-coating with 4000 rpm for 20 s. Ag (~100 nm) was evaporated onto PDINN layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective device area is 0.04 cm². The thickness of all films were measured by the Bruker Dektak-XT.

Electron-only devices

The structure for electron-only device is ITO/ZnO/active layer/Ca/Al. The ZnO precursor was spin-coated onto the ITO glass and annealed at 200 °C in air for 30 min. A donor:L8-BO blend in CHCl₃ with 1-Bromo-3,5-dichlorobenzene (D:A ratio = 1:1.8 (w/w)) was spin-coated (3000 rpm in N₂ for 30 s) onto the ZnO layer. Ca (~15 nm) and Al (~60 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

Hole-only devices

The structure for hole-only device is ITO/PEDOT:PSS/active layer/MoO₃/Ag. PEDOT:PSS layer (~30 nm) was made by spin-coating an aqueous dispersion onto the ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A donor:L8-BO blend in CHCl₃ with 1-Bromo-3,5-dichlorobenzene (D:A ratio = 1:1.8 (w/w)) was spin-coated (3000 rpm in N₂ for 30 s) onto the PEDOT:PSS layer. Then the film was annealed at 100 °C in N₂ for 10 min. Finally, MoO₃ (~3 nm) and Ag (~100 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

References

- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, F.D. Williams, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, Jr.J.A. Montgomery, J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, Fox, D. J. Gaussian 16, revision A.03; Gaussian, Inc.: Wallingford, CT, 2016.
- [2] P. Gawrys, T. Marszalek, E. Bartnik, M. Kucinska, J. Ulanski, M. Zagorska, Org. Lett. 2011, 13, 6090-6093.
- [3] J. Wang, C. Zhao, L. Zhou, X. Liang, Y. Li, G. Sheng, Z. Du, J. Tang, *Macromol. Rapid Commun.* 2021, 42, 2000757.